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CRYSTALLIZATION OF REDUCED STRONTIUM AND BARIUM NIOBATE PEROVSKITES FROM BORATE FLUXES.

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ABSTRACT

Single crystals of three A_xNbO_3 (A = Sr, Ba) reduced niobate cubic perovskites have been obtained by recrystallization of reduced ternary ceramic precursors from borate fluxes under high-vacuum. Product formation could be influenced by variation of the alkaline-earth metal oxide content of the flux, as well as the ternary precursor. The crystallized compounds have been characterized by single crystal X-ray diffraction, showing them to be ideal cubic perovskites with no evidence for long range ordering of the vacancies in the partially occupied A-site.
MATERIALS INDEX: perovskite, niobate, strontium, barium

Introduction

Many reduced ternary early transition metal oxides exhibit interesting physical properties such as charge-density wave instabilities and superconductivity (1,2). Single crystals are desirable for measuring the physical properties of this type of compound. A useful crystal growth technique is fused salt electrolysis (e.g. of A_2MoO_4), which has been successfully applied to obtain reduced ternary tungstates, molybdates, and vanadates (3). For reduced niobates this technique is not applicable due to the lack of low-melting oxidized ternary precursors. Here we describe the formation of single crystalline A_xNbO_3 (A = Sr, Ba) perovskites from strontium and barium borate fluxes in high vacuum. Borate fluxes have been regularly employed in the crystallization of ferroelectrics and garnets (4), but rarely for reduced early transition metal compounds (5). The low volatility of borates $AO{\cdot}xB_2O_3$ (A = Sr, Ba) makes them suitable for use in high-vacuum, and their melting points and chemical properties can be varied with the AO : B_2O_3 ratio. This allows tuning of the product formation if the A-cation is also part of the reduced ternary system.

Experimental

Ceramic Sr_xNbO_3 samples were prepared by heating pressed pellets of freshly prepared SrO, NbO_2, and Nb_2O_5 in the appropriate stoichiometry, wrapped in molybdenum foil, to 1200°C in high vacuum (10^{-6}-10^{-7} Torr) for 48 h with one intermediate regrind. Ceramic A_xNbO_3 and $Sr_5Nb_4O_{14}$ precursors for the crystallizations were prepared more rapidly by adding 5 mol% of B_2O_3 mineralizer to the pressed pellets, followed by heating to 1100°C for 22 h in high vacuum. Borate fluxes $AO{\cdot}xB_2O_3$ (A = Sr, x = 2, 0.7; A = Ba, x = 0.8) were freshly prepared by heating $A(NO_3)_2$ and B_2O_3 mixed in the appropriate stoichiometry to 750°C for 18 h in air in an alumina crucible.

Crystallizations were performed by placing the ground mixture of reduced ceramic precursor and flux (in 1 : 1.2-1.5 weight ratio) in Mo-foil cups covered with a Mo-foil lid. The mixtures were heated in a high vacuum furnace (Centorr) to 400°C to remove traces of adsorbed water, and then to 1100°C (10^{-6}-10^{-7} Torr) for 0.5 h, followed by cooling at 8°C/h to 950°C. Residual flux was etched away using a dilute aquaeous HF solution.

Single crystal X-ray diffraction data were collected at 23°C on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated MoKα radiation and the NRCCAD program package (6). Calculations were carried out on an Alliant FX/80 computer using the NRCVAX structure package (7). Lattice parameters were determined from absolute 2θ values of high-angle ($64° < 2\theta < 85°$) reflections. A Gaussian integration absorption correction was carried out for all collected intensity data. Crystallographic and experimental data are listed in Table I, thermal parameters and A-site occupancies in Table II. Positional parameters are: Sr or Ba at (0,0,0), Nb at (1/2,1/2,1/2), O at (1/2,1/2,0).

Ceramic Investigations

Ceramics with composition Sr_xNbO_3 were first investigated in the 1950's (8,9), when it was established that a single phase cubic perovskite is formed for $0.70 < x < 0.95$. For $0.60 < x < 0.70$ two-phase mixtures of cubic perovskite and a tetragonal tungsten bronze (TTB) type phase, $Sr_3Nb_5O_{15}$ (i.e. $Sr_{0.6}NbO_3$) (10) are formed. The single phase perovskites are metallic conductors down to 4K and pressed pellet resistivity data for four compositions are shown in Figure 1. No relation is evident between the compositional parameter x and the absolute resistivity, as was also observed for cubic Eu_xNbO_3 perovskite ceramics (11).

The Ba_xNbO_3 ceramics have been much less investigated (8,12), but it appears that the cubic perovskite single phase region is much narrower than for the Sr-niobate perovskites. We observed that for $x < 0.95$ two-phase mixtures with the TTB compound $Ba_3Nb_5O_{15}$ (13) are formed. Previously, no single crystals of any of these reduced phases mentioned have been grown.

Crystallizations

Recrystallization of a ceramic with nominal composition $SrNbO_3$ (Nb^{4+}) from $SrO{\cdot}2B_2O_3$ yielded only disproponionation. Dull metallic multiple twins of a Sr-poor niobate (EDAX) were obtained. These were identified by X-ray diffraction as $SrNb_8O_{14}$, a strongly reduced orthorhombic niobate containing $[Nb_6O_{12}]O_6$ clusters (14). Colorless Nb-containing material was the only other product observed. In the reaction of NbO_2 with $BaO{\cdot}3B_2O_3$ we also observed a disproportionation, forming $BaNb_8O_{14}$ (15), as a side reaction (16).

The observed disproportionation reaction apparently favors crystallization of relatively Sr-poor species, and can be suppressed by increasing the SrO-content of the mixture. This can be achieved by changing the composition of the ceramic precursor, as well as that of the flux.

TABLE I.

Crystallographic Data

Formula	$Sr_{0.72}NbO_3$	$Sr_{0.86}NbO_3$	$Ba_{0.95}NbO_3$
Space group	Pm3m	Pm3m	Pm3m
Crystal size (mm)	0.13 x 0.13 x 0.13	0.06 x 0.06 x 0.06	0.20 x 0.16 x 0.12
a (Å)	3.9865(2)	4.0077(6)	4.0853(2)
V (Å^3)	63.35(1)	64.37(1)	68.182(4)
Z	1	1	1
D_c (g/cm^3)	5.530	5.580	6.778
μ MoKα (cm^{-1})	204.5	211.2	181.5
Scan type	$\theta/2\theta$	ω	ω
Refl. measured	1236	909	961
Independent refl.	95	131	137
Obsd refl ($I > 2.5\sigma(I)$)	94	128	137
Refined parameters	7	7	7
R	0.013	0.018	0.031
R_w ($w = 1/\sigma^2(F_o)$)	0.015	0.016	0.039

TABLE II.

Temperature Factors and A-site Occupancies
for A_xNbO_3 Perovskites.

$Sr_{0.72}NbO_3$

	occ	U11	U33	Biso
Sr	0.724(4)	0.879(18)		0.694(14)
Nb		0.501(11)		0.396(8)
O		1.56(6)	0.39(6)	0.92(4)

$Sr_{0.86}NbO_3$

	occ	U11	U33	Biso
Sr	0.857(5)	0.917(17)		0.724(8)
Nb		0.342(10)		0.270(5)
O		1.79(7)	0.37(6)	0.92(4)

$Ba_{0.95}NbO_3$

	occ	U11	U33	Biso
Ba	0.948(9)	0.795(24)		0.627(11)
Nb		0.53(3)		0.417(14)
O		0.97(10)	0.48(14)	0.64(8)

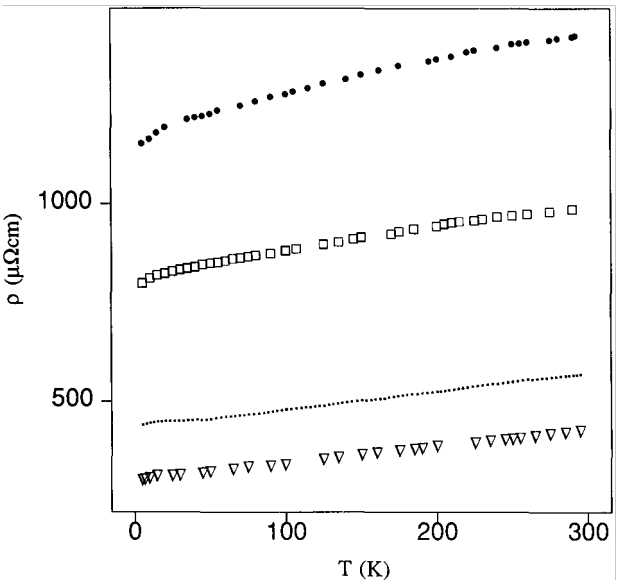

FIG. 1
Resistivity data for Sr_xNbO_3 perovskite ceramics; •, x = 0.80; ❑, x = 0.85; ·, x = 0.70; ∇, x = 0.90.

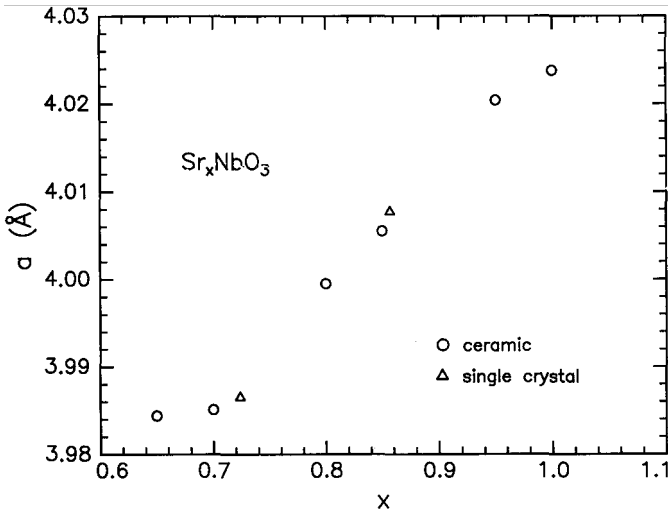

FIG. 2
Relationship between cell parameter *a* and compositional parameter x in Sr_xNbO_3 samples.

Recrystallization of the ceramic $Sr_5Nb_4O_{14}$ ($Nb^{4.5+}$) (17) from the same $SrO{\cdot}2B_2O_3$ flux still yielded some disproportionation, but also produced blue metallic-looking cubes of a perovskite, identified by single crystal X-ray diffraction as $Sr_{0.72}NbO_3$ ($Nb^{4.56+}$). Recrystallization of the $SrNbO_3$ (Nb^{4+}) ceramic from the SrO-rich flux $SrO{\cdot}0.7B_2O_3$ produced purple-red cubes of the perovskite $Sr_{0.86}NbO_3$ ($Nb^{4.28+}$), and no noticable $SrNb_8O_{14}$ formation. As a side product in this reaction, dark hexagons of the Sr-rich phase $Sr_5Nb_4O_{15-x}$ (17) were obtained, and identified by EDAX and unit cell determination on a single crystal.

Recrystallization of a ceramic with nominal composition $BaNbO_3$ (Nb^{4+}) from the Ba-rich borate $BaO{\cdot}0.8B_2O_3$ produced red metallic-looking crystalline aggregates of the cubic perovskite $Ba_{0.95}NbO_3$. As side product, dark blue metallic crystals of the TTB-phase $Ba_3Nb_5O_{15}$ were observed. Properties of single crystals of this phase will be reported elswhere (16). Remarkably, whereas the TTB-phase is ubiquitous in crystallization of Ba-Nb-O ceramics, we never observed crystallization of its Sr-analogue from borate fluxes. However, small single crystals of $Sr_3Nb_5O_{15}$ could be obtained by grain growth in a pressed pellet with 7 mol% of B_2O_3 added as a mineralizer (pellet heated at 1100°C for 48 h in high vacuum, cell parameters from single crystal X-ray diffraction: a = 12.3609(7) Å, c = 3.8974(3) Å).

X-Ray Structure Determinations

Single crystal X-ray structure determinations were performed on the three crystallized perovskite phases. Through refinement of the A-site occupancy, the compositions were determined to be $Sr_{0.72}NbO_3$, $Sr_{0.86}NbO_3$, and $Ba_{0.95}NbO_3$ (Table II) respectively. All three compounds appear to be ideal cubic disordered defect perovskites. High intensity (rotating anode generator) X-ray diffraction did not reveal any superstructure due to long-range order in the A-site vacancies. The cell parameter a in Sr_xNbO_3 increases with increasing x, and values for the single crystals fit well on the linear x versus a-curve observed for ceramic samples (Fig. 2), which follow Vegaards law in the single phase region (8). Deviations from this relation for perovskites in non-single phase ceramics ($x > 0.95$; $x < 0.70$) is clearly observed, defining the upper and lower limits for the Sr_xNbO_3 perovskites as 3.984 Å < a < 4.024 Å.

The cell parameter and composition of the Ba-niobate perovskite compare well with the values found by Svensson from Rietveld profile analysis on a Ba_xNbO_3 perovskite in a multi-phase ceramic, x = 0.97(3) and a = 4.0853(2) Å (18), confirming the narrow stability range of the Ba_xNbO_3 cubic perovskite phase.

Conclusions

Alkaline earth metal borates are useful fluxes for the crystallization of reduced ternary niobates. Variation of the SrO-content of the flux and SrO-content and average Nb oxidation state of the reduced ternary precursor enable the growth of crystals of Sr_xNbO_3 in different parts of the solid solution range. The low volatility of the Sr- and Ba-borates makes it possible to perform the crystallizations under high-vacuum conditions. Still, some partial oxidation of the mixture is observed, and use of freshly prepared borates is imperative. The crystals grown so far have been fairly small (cubes of 0.3-0.4 mm along the side), but growth of larger crystals should be possible under well-chosen conditions. Other results in the Ba-Nb-O (16), Sr-Ti-O and La-Ti-O systems (19) suggest the method may be more generally applicable for the crystallization of reduced ternary early transition metal oxides.

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